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AN ASSESSMENT OF A PROCESS FOR THE SOLIDIFICATION AND STABILIZATION OF LIQUID INDUSTRIAL WASTES

1976

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Ministry
of the
Environment

Ontario

The Honourable
George A. Kerr, Q.C.,
Minister

Everett Biggs,
Deputy Minister

Date Due

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AND
STABILIZATION OF LIQUID INDUSTRIAL WASTES

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Industrial Section
Pollution Control Branch

Ontario Ministry of the Environment
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AN ASSESSMENT OF A PROCESS FOR THE SOLIDIFICATION AND STABILIZATION OF LIQUID INDUSTRIAL WASTES

Introduction

In the spring of 1976, the Pollution Control Branch of the Ontario Ministry of the Environment evaluated a process for solidifying and stabilizing acidic "metal-bearing" liquid industrial wastes and the potential for landfill disposal of the processed material. The process was developed by David Krofchak Limited and Ontario Liquid Waste Disposal Limited (both of Cambridge, Ontario). During the trials, over 50,000 imperial gallons of the waste were solidified by the company and then stockpiled for observation and analytical testing.

The following conclusions, analyses and observations in this report apply only to the specific mixes prepared and supplied by the company.

Conclusions

(1) The solidification process appeared to hold and stabilize most of the heavy metals contained in the liquid waste. Heavy metal values in the leachates (laboratory and field) were commonly below 1 mg/litre;

(2) Leachates from the testing of processed material contained high concentrations of dissolved solids;

(3) The bulk of the common heavy metals present in the waste were retained in the processed material during extended periods of leaching with distilled water when considered on on a mass basis. Losses of heavy metals were relatively minor;

(4) Landfilling may be used to dispose of the processed material providing adequate facilities are available for the collection and treatment of leachate and run-off. The concern over dissolved solids contamination will dictate the adequancy of the facilities required.

Typical Chemical Characteristics of the Liquid Waste Used

See Appendix A

Analytical Testing of Solidified Wastes

The leachability of the solids resulting from the program was determined in the laboratory using distilled water.

Leach times varied and were commonly 24, 48, 72, 96 and 120 hours. A few tests were conducted over periods in excess of 500 hours.

Both saturated and unsaturated leach conditions were employed during the testing:

"saturated condition" - the sample being tested was fully immersed in the leach liquid for the duration of the test "unsaturated condition" - the leach liquid was introduced to the sample being tested drop by drop for the duration of the test

The volume of leach liquid used in each test was related to local (Southern Ontario) levels of precipitation (76 to 81 cm. rainfall per annum).

The weight of each representative sample being tested was normally between 100 and 500 grams.

The physical nature of the samples being leached was varied as much as possible. Some samples took the form of solid uniform cores of various diameters. Other samples were in the shape of small regular cones. Most samples, however, were simply in various states of subdivision. The most common sample consisted of angular fragments having diameters in the 2 to 3 centimeter range.

In addition, natural run-off from the stored material was collected on-site and evaluated.

Composition of Test Batches

Six test batches are referred to in this report. Due to the confidential nature of the project, specific details of the test batches may only be obtained from the company.

For the purposes of this report, the following test batches should be regarded as more or less identical or comparable:

Mix No. 1
Mix No. 4
Mix No. 5
Mix No. 6

The chemical composition of solidified samples is shown in Appendix D. Analytical results of laboratory leaching tests are detailed in Appendix B and in general may be considered acceptable except for dissolved solids.

Analytical Results of Actual Run-off (Leachate) Found on the Storage Site

Completed test batches were stored on the site in the open on an impermeable pad. The storage pad was designed to collect and channel any leachate or run-off due to rain to a common point where the leachate could be chemically treated and/or sampled.

During the month of May, natural run-off from the site was sampled on two occasions. The sample results are reported in Appendix C.

The results indicate acceptable levels of metals.

OBSERVATIONS BASED ON LABORATORY LEACHING TESTS

The following observations are based on the analytical results of Mix No. 1, Mix No. 4, Mix No. 5, and Mix No. 6 (see Appendix B). As indicated previously, these mixes are somewhat similar in composition, and therefore, should exhibit somewhat similar leachate results and should reflect the soundness of the system as a whole:

Observation A

The following represent the maximum, minimum and "average" concentrations of the substances and parameters being noted during this study that appeared in laboratory leachates during the first 24 to 72-hour period of leaching with distilled water:

	Maximum Concentration	Minimum Concentration	"Average" Concentration
pH	12.2	10.1	11.1
Conductivity (umhos/cm)	58,000	16,000	30,125
Cl^- (mg/litre)	23,500	2,040	9,625
SO_4 (mg/litre)	9,000	5,100	6,556
Mn (mg/litre)	.20	.05	.10
Cu (mg/litre)	.16	.06	.10
Zn (mg/litre)	.66	.05	.21
Pb (mg/litre)	.39	$<$.04	.15
Cd (mg/litre)	$<$.01	$<$.01	$<$.01
Ni (mg/litre)	.53	.05	.33
Fe (mg/litre)	.56	.21	.39
Cr (mg/litre)	.38	.06	.16

Observation B

The following represent the maximum, minimum and "average" concentrations of the substances and parameters being noted during this study that appeared in laboratory leachates after approximately 120 hours of leaching with distilled water:

	Maximum Concentration	Minimum Concentration	"Average" Concentration
pH	11.3	8.5	9.9
Conductivity (umhos/cm)	14,000	2,150	4,083
Cl^- (mg/litre)	900	44	201
SO_4 (mg/litre)	3,400	1,400	1,622
Mn (mg/litre)	.03	.02	.02
Cu (mg/litre)	.03	.02	.02
Zn (mg/litre)	.58	.02	.17
Pb (mg/litre)	.28	<.04	.08
Cd (mg/litre)	<.01	<.01	<.01
Ni (mg/litre)	.06	<.04	.04
Fe (mg/litre)	.21	.05	.10
Cr (mg/litre)	.08	<.04	.04

Observation C

The analytical "average" results quoted in Observation A and Observation B are comparable as follows:

	Average Concentration After 24 to 72 Hours Leaching	Average Concentration After 120 Hours Leaching
pH	11.1	9.9
Conductivity (umhos/cm)	30,125	4,083
Cl^- (mg/litre)	9,625	201
SO_4 (mg/litre)	6,556	1,662
Mn (mg/litre)	.10	.02
Cu (mg/litre)	.10	.02
Zn (mg/litre)	.21	.17
Pb (mg/litre)	.15	.08
Cd (mg/litre)	<.01	<.01
Ni (mg/litre)	.33	.04
Fe (mg/litre)	.39	.10
Cr (mg/litre)	.16	.04

All components indicated above of the leachate show decreasing concentrations with time.

Observation D

	Short-term Leachate Observed in Laboratory	Short-term Leachate Observed in Field
pH	11.1	11.8
Conductivity (umhos/cm)	30,125	62,000
Cl^- (mg/litre)	9,625	22,300
SO_4 (mg/litre)	6,556	6,100
Mn (mg/litre)	.10	.15
Cu (mg/litre)	.10	.20
Zn (mg/litre)	.21	.64
Pb (mg/litre)	.15	<.04
Cd (mg/litre)	<.01	<.01
Ni (mg/litre)	.33	.23
Fe (mg/litre)	.39	1.3
Cr (mg/litre)	.16	.30

Simple leaching with distilled water in a laboratory cannot simulate the complex conditions of the field. However, the trends observed in the laboratory should be noticeable in the field.

With a few exceptions, the concentrations of metals etc., noted in leachates in the field exceeded laboratory predictions by an average factor of approximately 2.4.

APPENDIX A

TYPICAL CHEMICAL CHARACTERISTICS OF THE LIQUID WASTE USED

pH	1.4
Total Solids	168,290 mg/litre
Dissolved Solids	167,900 mg/litre
Conductivity (umhos/cm)	225,000
Acidity	84,000 mg/litre ($CaCO_3$)
Nitrate Nitrogen (expressed as N)	8 mg/litre
Nitrite Nitrogen (expressed as N)	152 mg/litre
Ammonia Nitrogen (expressed as N)	120 mg/litre
Sulphates (as SO_4)	93,000 mg/litre
Chlorides (as Cl)	8,310 mg/litre
Calcium (as Ca)	474 mg/litre
Chromium (as Cr)	1,112 mg/litre
Copper (as Cu)	64 mg/litre
Iron (as Fe)	15,272 mg/litre
Manganese (as Mn)	164 mg/litre
Nickel (as Ni)	102 mg/litre
Zinc (as Zn)	greater than 11,000 mg/litre
Cadmium (as Cd)	9 mg/litre
Lead (as Pb)	21 mg/litre
Vanadium (as V)	less than 2 mg/litre

APPENDIX B

ANALYTICAL RESULTS OF LEACHING TESTS

General Notes

(i) All samples referred to in this section were leached with distilled water at room temperature;

(ii) The time, volume and physical and chemical parameters shown in this section are recorded as follows:

Time (hours)	48	120
Volume (mls)	300	350
Zn (mg/litre)	.66	.50

etc.

In the above, leaching with distilled water commenced at time "zero". After 48 hours of continuous leaching the total leachate volume (300 mls) up to that time was collected and analyzed. The leachate contained .66 mg/litre Zn. Leaching continued and after 120 hours (from time "zero") another leachate cut was taken (350 mls). The 350 mls taken represented the total volume of leachate collected during the time interval between 48 and 120 hours. This cut contained .50 mg/litre Zn. The total volume of leachate taken for the entire 120 hour test was 300 + 350 = 650 mls.

(A) RESULTS: MIX NO. 1

Date Mixed on Site: April 6, 1976
Date Leach Test Commenced: April 21, 1976

Sample Description:

Sample (a)	2.5 cm fragments; saturated flow
Sample (b)	granular; saturated flow
Sample (c)	2.5 cm fragments; unsaturated flow
Sample (d)	granular; unsaturated flow

NOTE:

The above weights included an average of 35% water.

The long term effects of leaching were investigated using sample (c). Leaching was carried out under unsaturated leach conditions. At the end of 120 hours (from time "zero"), the sample was allowed to age (sit undisturbed) in the leaching column for 20 days. During this period the sample may have been damp but it was not sitting in water. At the end of the twenty-day period leaching resumed as if the aging period had not occurred. Leaching ceased after 552 hours (from time "zero").

	Saturated Flow				Unsaturated Flow			
Sample	a	a	b	b	c	c	d	d
Time (hours)	48	120	48	120	48	120	48	120
Volume (mls)	450	600	450	600	300	350	300	450
pH	12.2	11.1	11.7	10.5	12.1	11.3	11.5	10.4
Conductivity (umhos/cm)	35,000	8,000	28,000	4,000	58,000	14,000	41,000	4,400
Cl^- (mg/litre)	9,070	690	5,200	160	6,410	900	8,955	260
SO_4 (mg/litre)	5,100	1,500	5,500	1,400	7,700	3,400	9,000	2,000
Mn (mg/litre	.07	.02	.05	.02	.19	.03	.08	.02
Cu (mg/litre)	.06	<.02	.08	.02	.16	.03	.10	.02
Zn (mg/litre)	.50	.40	.33	.58	.66	.50	.14	.08
Pb (mg/litre)	<.04	.06	.06	.13	.39	.28	<.04	<.04
Cd (mg/litre)	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Ni (mg/litre)	.05	.06	.06	.05	.10	<.04	.05	<.04
Fe (mg/litre)	.21	.21	.22	.18	.39	.17	.24	.15
Cr (mg/litre)	.06	<.04	.08	.05	.12	.07	.27	.08

Unsaturated Flow

Sample	c	c	c	c	c	c	c	c
Time (hours)	48	120	192	216	288	300	432	552
Volume (mls)	300	350	300	200	450	450	450	500
pH	12.1	11.3	12.1		11.9	11.9	11.9	11.9
Conductivity (umhos/cm)	58,000	14,000	5,200		3,500	3,200	3,100	3,500
Cl^- (mg/litre)	6,410	900	395	297				
SO_4 (mg/litre)	7,700	3,400	610	440			240	
Zn (mg/litre)	.66	.50	.18	2.17		.03	.03	.02
Cr (mg/litre)	.12	.07	.04	.38		.05	.14	<.04
Cu (mg/litre)	.16	.03	.03	.04				
Ni (mg/litre)	.10	<.04	.04	.09				
Pb (mg/litre)	.39	.28	.17	.07				
Mn (mg/litre)	.19	.03	.04	.02				
Fe (mg/litre)	.39	.17	.6	.6				
Na (mg/litre)	3,460	89			9			
K (mg/litre)	25,000	3,100			330			

(B) RESULTS: MIX NO. 2

Date Mixed on Site: April 14-15, 1976
Date Leach Test Commenced: April 23, 1976

Sample Description:

representative lumps approximately 2.5 cm in diameter

Weight of Sample:

308 gms (approximately 35% water)

	Unsaturated flow	Unsaturated flow	Saturated flow
Time (hours)	72	96	120
Volume (mls)	100	50	300
pH	8.8	8.8	11.1
Conductivity (umhos/cm)	60,000	46,500	1,180
Cl^- (mg/litre)	7,300	19,880	94
SO_4 (mg/litre)	7,400	12,500	340
Mn (mg/litre)	.14	.09	<.02
Cu (mg/litre)	.21	.21	<.02
Zn (mg/litre)	.12	.12	.04
Pb (mg/litre)	<.04	<.04	.10
Cd (mg/litre)	<.01	<.01	<.01
Ni (mg/litre)	.49	.33	<.04
Fe (mg/litre)	.53	.25	.26
Cr (mg/litre)	.12	.07	.06
Co (mg/litre)	------	------	<.04
As (ugm/litre)	<2	<2	<2

(C) RESULTS: MIX NO. 3

Date Mixed on Site: April 14-15, 1976
Date Leach Test Commenced: April 23, 1976

Sample Description:

representative lumps approximately 2.5 cm in diameter

Weight of Sample:

276 grams (approximately 35% water)

	Unsaturated flow	Unsaturated flow	Saturated flow
Time (hours)	72	96	120
Volume (mls)	150	50	300
pH	8.7	8.7	9.4
Conductivity (umhos/cm)	43,000	25,500	4,650
Cl^- (mg/litre)	5,020	------	227
SO_4 (mg/litre)	12,000	9,500	2,200
Mn (mg/litre)	.09	------	.02
Cu (mg/litre)	.45	------	.05
Zn (mg/litre)	.12	------	.04
Pb (mg/litre)	<.04	------	<.04
Cd (mg/litre)	<.01	------	<.01
Ni (mg/litre)	.71	------	.06
Fe (mg/litre)	.27	------	.18
Cr (mg/litre)	.04	------	<.04
Co (mg/litre)	------	------	<.04

(D) RESULTS: MIX NO. 4

Date Mixed on Site: April 14-15, 1976
Date Leach Test Commenced: April 23, 1976

Sample Description:

representative lumps approximately 2.5 cm in diameter

Weight of Sample:

284 grams (approximately 35% water)

	Unsaturated flow	Unsaturated flow	Saturated flow
Time (hours)	72	96	120
Volume (mls)	300	150	300
pH	11.8	11.8	10.3
Conductivity (umhos/cm)	32,000	6,400	2,500
Cl^- (mg/litre)	23,350	600	57
SO_4 (mg/litre)	6,900	2,350	1,430
Mn (mg/litre)	.07	.02	<.02
Cu (mg/litre)	.10	.06	<.02
Zn (mg/litre)	.30	.07	.10
Pb (mg/litre)	.38	.06	.06
Cd (mg/litre)	<.01	<.01	<.01
Ni (mg/litre)	.27	<.04	.04
Fe (mg/litre)	.28	.19	.07
Cr (mg/litre)	.07	<.04	<.04
Co (mg/litre)	------	------	<.04

(E) RESULTS: MIX NO. 5

Date Mixed on Site: April 19, 1976
Date Leach Test Commenced: April 23, 1976

Sample Description:

representative lumps approximately 2.5 cm in diameter

Weight of Sample:

265 grams (approximately 35% water)

	Unsaturated flow	Unsaturated flow	Saturated flow
Time (hours)	72	96	120
Volume (mls)	300	150	300
pH	11.0	11.3	8.5
Conductivity (umhos/cm)	32,000	4,000	2,150
Cl^- (mg/litre)	2,040	349	44
SO_4 (mg/litre)	7,400	1,800	1,480
Mn (mg/litre)	.20	.02	.02
Cu (mg/litre)	.13	.04	.02
Zn (mg/litre)	.10	.02	.02
Pb (mg/litre)	<.04	<.04	<.04
Cd (mg/litre)	<.01	<.01	<.01
Ni (mg/litre)	.53	<.04	.04
Fe (mg/litre)	.56	.14	.05
Cr (mg/litre)	.06	.06	<.04
Co (mg/litre)	------	------	<.04

(F) RESULTS: MIX NO. 6

Date Mixed on Site: April 22, 1976
Date Leach Test Commenced: April 26, 1976

Sample Description:

original slurry poured into cone-shaped mould; slurry allowed to harden. Approximate dimensions of cone: base 5.5 cm; height 8 cm

Weight of Sample:

75 grams (approximately 35% water)

	Unsaturated flow	Unsaturated flow
Time (hours)	24	48
Volume (mls)	150	250
pH	10.1	9.5
Conductivity (umhos/cm)	16,000	4,750
Cl^- (mg/litre)	5,550	387
SO_4 (mg/litre)	5,100	2,200
Mn (mg/litre)	.05	.02
Cu (mg/litre)	.10	.03
Zn (mg/litre)	.05	.03
Pb (mg/litre)	<.04	<.04
Cd (mg/litre)	<.01	<.01
Ni (mg/litre)	.46	.05
Fe (mg/litre)	.44	.22
Cr (mg/litre)	.38	.11
Co (mg/litre)	------	<.04

APPENDIX C

ANALYTICAL RESULTS OF ACTURAL RUN-OFF (LEACHATE) FOUND ON THE STORAGE SITE

(a) May 7, 1976

Run-off due to precipitation occurred at the storage site on May 7, 1976. The volume of run-off from the pad was estimated to be 4.5 litres/minute. Samples were taken and the analytical results were as follows:

Solids (mg/litre)	Total	Suspended	Dissolved
Dried	50,565	225	50,340
Ashed	49,365	200	49,165
Loss	1,200	25	1,175

pH - 11.8

Conductivity (umhos/cm) - 62,000

Alkalinity (mg/litre of $CaCO_3$) - 619 (OH-505; CO_2-114; HCO_3-0)

Cl^- (mg/litre) - 22,300

SO_4 (mg/litre) - 6,100

Nitrite (as N) (mg/litre) - .02

Nitrate (as N) (mg/litre) - 2.4

Ammonia (as N) (mg/litre) - 6.3

Total P (mg/litre) - .06

Na (mg/litre) - 3,200

K (mg/litre) - 20,000

Ca (mg/litre) - 1,000

Cu (mg/litre) - .20

Ni (mg/litre) - .23

Pb (mg/litre) - $<$.04

.....continued

Zn (mg/litre) - .64

Cd (mg/litre) -<.01

Cr (mg/litre) - .30

Mn (mg/litre) - .15

Fe (mg/litre) - 1.3

Co (mg/litre) - .04

Mo (mg/litre) - 1.1

(b) May 11, 1976

On May 11, 1976, active run-off was not occurring at the site. However, pools of water sitting on the pad served as an indication that run-off had occurred. These pools were sampled and the analytical results were as follows:

pH - 7.2
Conductivity (umhos/cm) - 19,000
Cl^- (mg/litre) - 4,389
SO_4 (mg/litre) - 2,800
Nitrite (as N) (mg/litre) - .24
Nitrate (as N) (mg/litre) - 2.2
Ammonia (as N) (mg/litre) - .2
Total P (mg/litre) - .4
Na (mg/litre) - 730
K (mg/litre) - 4,600
Ca (mg/litre) - 47
Cu (mg/litre) - .05
Ni (mg/litre) - .09
Fe (mg/litre) - .8
Zn (mg/litre) - .33
Cd (mg/litre) - $<$.01
Cr (mg/litre) - .15
Mn (mg/litre) - .03
Mg (mg/litre) - 7.2

APPENDIX D

CHEMICAL COMPOSITION OF SOLIDIFIED SAMPLES BEFORE LABORATORY LEACHING

		Mix #2	Mix #3	Mix #4	Mix #5
Al	mg/gm	14	8.9	11	12
Cd	ug/gm	0.5	1.1	1.1	.62
Ca	mg/gm	130	131	145	116
Cr	ug/gm	510	110	130	1,400
Co	ug/gm	8	4.9	6.8	9.8
Cu	ug/gm	27	28	34	43
Fe	mg/gm	28	39	31	39
Pb	ug/gm	79	110	500	64
Mg	mg/gm	9	5.6	7.7	8.3
Mn	ug/gm	380	340	410	440
Ni	ug/gm	46	43	40	95
Zn	ug/gm	5,100	28,000	11,000	12,000

NOTE:

The above results (ug/gm or mg/gm) were on a dry weight basis. All water was driven from the samples before analysis.

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